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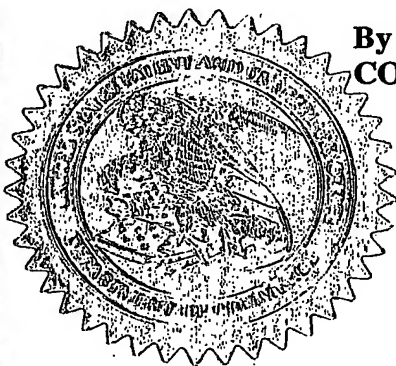
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 Name: Mark J. Jankers

REQUEST FOR PROVISIONAL APPLICATION UNDER 37 C.F.R. § 1.53(c)

**BOX PROVISIONAL PATENT APPLICATION**
 Commissioner for Patents  
 Washington, DC 20231

Dear Sir:

This is a request for filing a Provisional application for patent under 37 CFR § 1.53(c) entitled **PIGMENT AGGLOMERATES, THEIR MANUFACTURE, AND THEIR USE** by the following inventor(s):

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- ☒ Enclosed is the Provisional application for patent as follows: 9 pages of specification, 13 claims, 1 page of Abstract, and 1 sheet of drawings.
- ☒ Small entity status is claimed pursuant to 37 CFR 1.27.
- ☒ Payment of Provisional filing fee under 37 C.F.R. § 1.16(k) :
  - ☒ Attached is a check in the amount of \$80.00.
  - ☐ Please charge Deposit Account No. 13-2725.
  - ☐ PAYMENT OF THE FILING FEE IS BEING DEFERRED.
- ☒ The Commissioner is hereby authorized to charge any additional fees as set forth in 37 CFR §§ 1.16 to 1.18 which may be required by this paper or credit any overpayment to Account No. 13-2725.
- ☐ Enclosed is an Assignment of the invention to \_\_\_\_\_, Recordation Form Cover Sheet and a check for \$ \_\_\_\_\_ to cover the Recordation Fee.
- ☐ Also Enclosed:
- ☐ The invention was made by the following agency of the United States Government or under a contract with the following agency of the United States Government:

8. ☒ Address all future communications to the Attention of Mara E. Liepa (may only be completed by attorney or agent of record) at the address below.
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Respectfully submitted,

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**PIGMENT AGGLOMERATES, THEIR MANUFACTURE, AND THEIR USE**

The present invention is directed to pigment agglomerates for use in coloring concrete and other cementitious products, and methods for making the pigment particles.

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**Background of the Invention**

Common, gray concrete is used extensively throughout the construction and building industries and is generally the norm. However, many industries which utilize concrete and other cementitious products such as mortars and grouts are adding a coloring agent, such as a pigment, to the concrete or cementitious product. For ease of description herein, such cementitious products will be referred to simply as concrete or concrete products, it being understood that such simple terminology is intended to refer to the broader category of cementitious products. The pigment can be either mixed into the wet concrete prior to pouring or can be topically applied to the concrete after pouring.

Iron oxide, which is available in various colors as a powder, is one common pigment for use with concrete. In order to provide a wide range of colors, a supplier will custom mix multiple base colors of pigment to obtain the desired final shade. One common problem with iron oxide, and other pigments, is that the pigment powder is difficult to handle. The powders have a tendency to clump, which causes irregular flow during conveyance (such as transporting with an auger, dumping, etc.).

There are many commercially available pigment products that have attempted to address the problems of clumping. For example, HG Starck, a division of Bayer Company, produces a compressed powdered pigment. Davis Colors has a competing pigment line, which uses pigment granules of iron oxide color particles that are combined with a binder material. These pigment granules are not compacted or briquetted granules. See U.S. Patent No. 4,946,505 (Jungk).

25

What is desired is an improved coloring product for use in concrete.

### Summary of the Invention

The invention is directed to a method of making particulate pigment for use in coloring concrete products. The particulate pigment product is an agglomerate of pigment particles and at least one carrier particle. The carrier particle acts as a nucleus  
5 for the agglomerate.

In one aspect of the invention, a pigment agglomerate consisting of at least one carrier particle and a plurality of pigment particles is provided. In a preferred aspect, the carrier particle is a silica particle, such as silica fume. In another preferred aspect, either additionally or alternately to the former preferred aspect, the pigment particles are  
10 iron oxide particles. In a preferred aspect, the pigment agglomerate consists essentially of a weight ratio of about 1:10 to 3:10 carrier particles : pigment particles.

The invention is also directed to methods of making pigment agglomerates. The method mixes together carrier particles and pigment particles, preferably at a weight ratio of about 1:100 to 3:10 (carrier particles : pigment particles),  
15 the mixing being done in a tumbling or rotary motion. No polymeric binder or other binder material is needed to provide the pigment agglomerates. Rather, the carrier particles and pigment particles form generally spherical agglomerates that are held together by interparticle forces. By the term "interparticle forces", what is intended is a force that originates in one particle and acts upon a force in another particle or upon the  
20 other particle itself.

Pigment agglomerates have improved flowability over non-agglomerated pigments. For example, an agglomerate consisting of silica fume and iron oxide is easier to handle (e.g., pour, auger, transport) than iron oxide without the silica fume carrier.

When exposed to a concrete mix (i.e., the cement, sand, water, etc), it is  
25 believed that the pigment agglomerate is destroyed and the pigment particles disperse homogenously throughout the concrete. Additionally, the carrier particle may impart beneficial properties to the concrete.

**Brief Description of the Drawings**

Figure 1 is a schematic perspective view of a pigment agglomerate according to the invention;

Figure 2 is an enlarged, cross-sectional view of a first variation of the pigment agglomerate of Figure 1; and

Figure 3 is an enlarged, cross-sectional view of a second variation of the pigment agglomerate of Figure 1.

**Detailed Description**

Referring to the figures, wherein like numerals represent like elements throughout the several views, there is schematically illustrated in Figures 1, 2 and 3, a pigment agglomerate 10. Pigment agglomerate 10 is formed by a plurality of pigment particles 12 and at least one carrier particle 14. Carrier particles 14 are illustrated in Figures 2 and 3 as being shaded. This shading is merely to facilitate understanding of the invention and to differentiate between pigment particles 12 and carrier particles 14, and is not intended to limit the coloring or such of carrier particles 14. As seen in Figure 2 and 3, carrier particle 14 is present within an interior of agglomerate 10 and is surrounded by, and typically covered by, pigment particles 12. In Figure 2, agglomerate 10 has one carrier particle 14 and a plurality of pigment particles 12. In Figure 3, agglomerate 10 has multiple carrier particles 14 and a plurality of, or multiple, pigment particles 12. In the illustrated agglomerates 10, carrier particles 14 are internal particles, that is, they are not present on the exterior surface of agglomerate 10. However, in some agglomerates 10, a carrier particle 14 may form a portion of an exterior surface of agglomerate 10, although typically, carrier particle 14 will be surrounded by pigment particles 12, as illustrated in Figures 2 and 3.

The weight ratio of carrier particles 14 to pigment particles 12, in pigment agglomerate 10, is at least 5 to 100, and preferably at least 10 to 100. The ratio is no greater than 50 to 100, and preferably no greater than 30 to 100. It is believed that if the ration of carrier particles 14 is too great in agglomerate 10,

Agglomerates 10 are held together, that is, pigment particles 12 are held to carrier particles 14, by interparticle forces that occurs between particles 12 and particles 14. That is, no polymeric binder (also commonly referred to as an adhesive) or other such additive is used to bind pigment particles 12 to carrier particles 14.

5           For example, carrier particle 14 may have a naturally occurring positive charge, and when combined with pigment particles 12 having a negative charge, particles 14 and 12 have a tendency to be attracted to each other. As another example, static electric charges or forces may attract and hold together particles 12 and 14.

          As stated above, pigment particles 12 are bound to carrier particles 14 by  
10   interparticle forces such as magnetic forces, electrostatic forces, van der Waal's forces, and other physical or chemical interparticle forces. At the time of this filing, it is not understood what forces hold pigment particles 12 and carrier particle 14 together as agglomerate 10, however it is known that the two particles 12 and 14 do not chemically react with one another, and the resulting agglomerate 10 retains discrete pigment particles  
15   12 and carrier particles 14. When agglomerate 10 is destroyed, for example, by crushing, excessive shaking or application of harsh forces, agglomerate 10 breaks down to pigment particles 12 and carrier particles 14. If one were to have the patience and time, one could literally separate particles 12 from particles 14.

          The interparticle forces that hold agglomerate 10 together can be either a  
20   naturally occurring characteristic of pigment particle 12, carrier particle 14, or both, or, the interparticle forces may be the result of a treatment or the like applied to the particle(s).

          The charge of a particle, either of pigment particles 12 or carrier particles 14, may be enhanced or altered by pre-treating the particles with a surfactant or other  
25   similar, non-polymeric additive. For example, a naturally occurring positive charge on carrier particle 14 can be enhanced by a cationic surfactant, and/or a naturally occurring negative charge on pigment particle 12 can be enhanced by an anionic surfactant.

          Examples of suitable surfactants include those available under the trade designation "Tween" from ICI Surfactants. Both anionic and cationic surfactants are  
30   available from Goldschmidt Chemical Company, and from Fiber-Shield Industries, Inc.

Other procedures of enhancing the charge differential of pigment particles 12 and carrier particles 14 could also be used, including methods as simple as applying a static or magnetic charge to the particles by electricity or magnets.

As stated above, it is not understood what forces hold pigment particles 12 and carrier particle 14 together. Other interparticle enhancing procedures could be used to enhance the interparticle forces, depending on what the interparticle forces holding agglomerate 10 together are.

Agglomerates 10 generally have a size at least about 0.1 mm in diameter and more usually at least about 0.5 mm in diameter. Often, the diameter is at least 1 mm. Agglomerates 10 generally have a size no more than about 5 mm in diameter and often no more than about 4 mm.

#### Pigment Particles

Pigment particles 12 that may be suitable in agglomerates 10 of the invention for coloring concrete, or that may be suitable for forming agglomerates 10 by the inventive method, include both inorganic and organic pigments that are in the form of a dry powder. Classes of inorganic pigments include metallic oxides (e.g., iron, titanium, zinc, cobalt, chromium), metal powers (e.g., gold, aluminum), earth colors (e.g., siennas, ochers, umbers), lead chromates, and carbon black. Classes of organic pigments include animal (e.g., rhodopsin, melanin), vegetable, (e.g., chlorophyll, xanthophylls, indigo, flavone, carotene).

Examples of pigment particles particularly believed to be suitable for incorporation into a pigment agglomerate include iron oxide, titanium dioxide, and carbon black. The preferred pigment particulate is iron oxide.

Iron oxide is typically available in various shades, ranging from yellow to red to almost black. The shade of the iron oxide is due to various contaminants and other additives present in the sample. Black iron oxide may also be referred to as ferrosferric oxide, ferroferric oxide, iron oxide (magnetic), or black rouge, or even magnetite. Black iron oxide may appear reddish or bluish-black. Brown iron oxide may also be referred to as iron subcarbonate, or iron carbonate, and is typically reddish-brown containing ferric



carbonate with ferric hydroxide  $\text{Fe}(\text{OH}_3)$  and ferrous hydroxide  $\text{Fe}(\text{OH}_2)$  in varying quantities. Metallic brown iron oxide is a naturally occurring earth, principally ferric oxide. Red iron oxide may also be referred to as burnt sienna, Indian red, red oxide, iron oxide red, rouge, or Turkey red, and is composed mainly of ferric oxide ( $\text{Fe}_2\text{O}_3$ ). Yellow  
5 iron oxide may also be referred to as iron oxide yellow, and is a hydrated ferric oxide,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . Typically, multiple source shades are combined to produce the desired shade.

#### Carrier Particle

10 As provided above, pigment agglomerates 10 are composed of pigment particles 12 and at least one carrier particle 14. Examples of suitable carrier particles 14 include silicas and oxides. An example of a preferred carrier particle 14 is silica fume, which is a by-product from semi-conductor or silicon wafer manufacturing processes. Silica fume is not fumed silica. More specifically, silica fume is a by-product of the  
15 manufacture of silicon alloys which are produced in submerged-arc electric furnaces. It is also collected during the production of other silicon alloys such as ferrochromium, ferromanganese, ferromagnesium, and calcium silicon.

Silica fume that is collected from waste gases without being treated is called "undensified silica fume;" this distinguishes it from other forms of silica fume that  
20 have been treated.

Undensified silica fume generally has particles of approximately 0.1 mm. It has a specific weight of about 200 to 300 kg/m<sup>3</sup>. To facilitate handling of silica fume, the industry often produces condensed silica fume, which is the product of further treated  
25 undensified silica fume, in which the particles are condensed until small spheres with diameters of about 0.5 to 1 mm are formed. The bulk density of the condensed silica fume is then increased to about 600 kg/m<sup>3</sup>. Condensed silica fume particles are mainly vitreous, and have a specific gravity of about 2.20. Condensed silica fume is primarily grayish in color, with levels varying from almost white to brownish-gray.

White amorphous silica fume is a highly reactive pozzolanic material and  
30 is known as a cement additive. It is able to alter the performance (e.g., compressive

strength) of a cementitious compound due to its high silica content, small particle size, and high surface area.

One white amorphous silica fume, commercially available from NorChem, generally is 81-89% silicon dioxide (silica,  $\text{SiO}_2$ ), has a moisture content of about 0.10-0.50%, has a specific gravity of about 2.20-2.70, a bulk density of about 38-44 lbs/ft<sup>3</sup>, and has an average particle size of about 0.9 micrometers and a surface area of about 10 m<sup>2</sup>/g.

Another white silica fume, available from NorChem, is about 85-93% amorphous silicon dioxide (silica), 6-13% zirconium dioxide (zirconia,  $\text{ZrO}_2$ ), 0.5-2% aluminum oxide (alumina,  $\text{Al}_2\text{O}_3$ ), an 0-6% calcium oxide (calcia,  $\text{CaO}$ )

Silica fume has been found to be a preferred carrier particle 14, at this time of this filing. It is not understood what characteristics make it more preferable over other carrier particles 14, including other silicas, tested at this time.

#### 15                    Manufacture of Pigment Agglomerates

The pigment agglomerates 10 of the invention are made by mixing together, with a rotary or rolling action, pigment particles 12 and carrier particles 14. Examples of equipment that provides suitable action for making agglomerates 10 include: barrel mixer, tumbler, ribbon blender, a slow running vane extruder, and even a sealable jar or barrel that can be rolled about its longitudinal axis. An air mixer, which uses air flow to move the particles, may additionally be a suitable mixing technique. The motion desired for making of agglomerates 10 is a rolling action optionally combined with an easy falling action. Minimal shear forces on particles 12, 14 or agglomerates 10 are desired. The process of making agglomerate 10 can be compared to rolling a snowball, starting with a central core and having it build-up as it rolls. For agglomerates 10, carrier particle 14 is analogous to the central core and pigment particles 12 build-up around carrier particle 14 as the material is rolled.

When making agglomerates 10, the weight ratio of carrier particles 14 to pigment particles 12 is at least 0.5 to 100, and preferably at least 1 to 100. As the ratio of carrier particles 14 reduces, it becomes more difficult to form and retain agglomerates 10.

The ratio of carrier particles 14 to pigment particles 12 is no greater than 50 to 100, and preferably no greater than 30 to 100.

It has been found that when using a higher level of carrier particles 14, the resulting agglomerates 10 are either (1) smaller in size (diameter) than if less carrier particles 14 were used, (2) are more difficult to destroy, for example, by imparting harsh shear forces on agglomerates 10, or (3) both.

#### Coloring of Concrete

The pigment agglomerates 10 of the invention facilitate the addition of pigment to copncrete and other cementitious products. Pigment agglomerates 10 have improved flowability over non-agglomerated pigment particles 12. Pigment particles 12, alone, have a tendency to clump, which can clog machinery and transport lines or tubes; this is especially the case for iron oxide. Providing pigment particles 12 with carrier particle 14 modifies the flow characteristics as compared to pigment particles 12 alone.

For example, agglomerates consisting of silica fume and iron oxide are easier to handle (e.g., pour, auger, transport) than iron oxide without the silica fume carrier. It has been found that iron oxide / silica fume agglomerates do not clump and provide less processing problems than iron oxide particles.

Use of agglomerates 10, which includes carrier particle 14, instead of straight pigment particles 12, typically does not detrimentally affect the coloring or shade of the concrete product. It should be understood that some agglomerates 10 may change the coloring characteristics, for example, if white or near-white pigment particles 12 are combined with a dark carrier particle 14, the resulting agglomerates 10 may have a darker color and provide the concrete with a darker color than pigment particles 12 alone. It has been found that silica fume, when used as carrier particle 14, generally does not affect the concrete color. However, this may differ if a dark gray silica fume or a high level of silica fume is used in agglomerates 10.

When exposed to a concrete mix (i.e., the cement, sand, water, etc), it is believed that pigment agglomerate 10 is destroyed, and pigment particles 12 disperse

homogenously throughout the concrete. Depending on the type of carrier particle 14 used, carrier particle 14 may impart beneficial physical properties to the concrete. For example, silica fume, when used by itself as an additive in concrete, increases the compressive strength of the concrete.

5

The foregoing description addresses embodiments of the present invention encompassing the principles of the present invention. The embodiments may be changed, modified and/or implemented using various types of arrangements. Those skilled in the art will readily recognize various modifications and changes which may be made to the present invention without strictly following the exemplary embodiments and applications illustrated and described herein, and without departing from the scope of the present invention.

10

1. A pigment agglomerate comprising:
  - (a) a plurality of pigment particles;
  - (b) at least one carrier particle; the plurality of pigment particles held to the at
- 5 least one carrier particle by interparticle forces, wherein the at least one the at least one carrier particle present has a weight ratio to the pigment particles of from about 1:10 to 3:10
2. the pigment agglomerate of claim 1, wherein the interparticle forces is at
- 10 least one of magnetic forces, electrostatic forces, and van der Waal's forces.
3. A pigment agglomerate consisting essentially of:
  - (a) a plurality of pigment particles; and
  - (b) at least one carrier particle.
- 15 4. A pigment agglomerate consisting of:
  - (a) a plurality of pigment particles; and
  - (b) at least one carrier particle.
- 20 5. The pigment agglomerate of any of claims 1, 2, 3 or 4 wherein the pigment particles are iron oxide.
6. The pigment agglomerate of any of claims 1, 2, 3, 4 or 5 wherein the at
- 25 least one carrier particle is silica fume.
7. A method of making a pigment agglomerate comprising:
  - (a) mixing a plurality of pigment particles with a plurality of carrier particles,
- at a weight ratio of 1:100 to 3:10 carrier particles to pigment particles, the mixing being done with a rolling motion.
- 30

8. The method of claim 7, wherein the mixing of a plurality of pigment particles with a plurality of carrier particles comprises:

(a) mixing a plurality of iron oxide particles with a plurality of silica fume particles.

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9. The method of claim 7, wherein the mixing of a plurality of pigment particles with a plurality of carrier particles consists of:

(a) mixing a plurality of iron oxide particles with a plurality of silica fume particles.

10

10. The method of claim 7, wherein the mixing of a plurality of pigment particles with a plurality of carrier particles with a rolling motion comprises:

(a) mixing of a plurality of pigment particles with a plurality of carrier particles with a rolling motion in a barrel mixer, a tumbler, or a ribbon mixer.

15

11. The method of claim 7, wherein the mixing of a plurality of pigment particles with a plurality of carrier particles with a rolling motion consists of:

(a) mixing of a plurality of pigment particles with a plurality of carrier particles with a rolling motion in a barrel mixer, a tumbler, or a ribbon mixer.

20

12. The method of claim 7, wherein the mixing of a plurality of pigment particles with a plurality of carrier particles with a rolling motion comprises:

(a) mixing of a plurality of pigment particles with a plurality of carrier particles with a rolling motion in a barrel spinning or tumbling about its longitudinal axis.

25

13. The method of claim 7, wherein the mixing of a plurality of pigment particles with a plurality of carrier particles with a rolling motion consists of:

(a) mixing of a plurality of pigment particles with a plurality of carrier particles with a rolling motion in a barrel spinning or tumbling about its longitudinal axis.

30

**Abstract**

A pigment agglomerate and method of making the pigment agglomerate.

The agglomerate is a collection of pigment particles and at least one carrier particle, the  
5 pigment particles and carrier particle held together by interparticle forces such as  
magnetic forces, electrostatic forces, van der Waal's forces, and other physical or  
chemical interparticle forces. A chemical surface treatment or other treatment may be  
applied to either or both of carrier particles and pigment particles in order to improve the  
interparticle forces therebetween. No binder, such as a polymeric binder or adhesive, is  
10 used to adhere or maintain the particles together forming the agglomerates.

FIG. 1

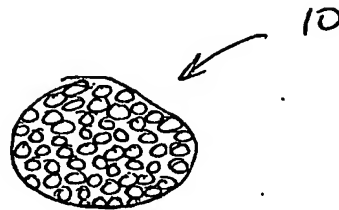


FIG. 2

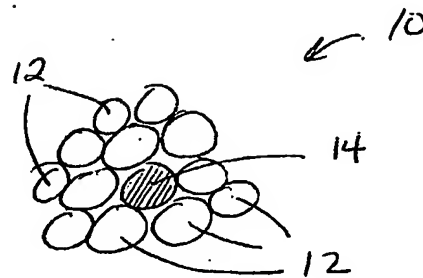
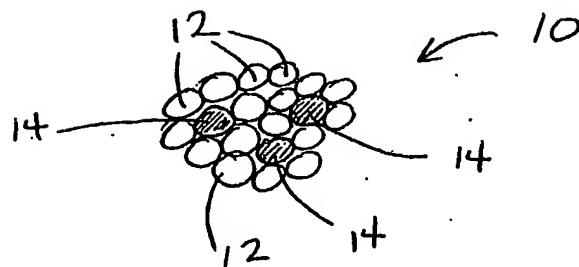


FIG. 3





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